The Synthesis of 1,2-Diazepines from Thiapyrylium Salts[1]

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The reactions of thiapyrylium salts **3***a–c* with hydrazine and methylhydrazine yield the 3,5,7-triphenyl-1,2(4*H*)-diazepines **4***a–c* and 1-methyl-3,5,7-triphenyl-1,2(1*H*)-diazepines **5***a–c* in good to excellent yields. Although numerous 1-acyl-1,2(1*H*)-diazepines are now known, compounds **5***a–c* represent the first examples of 1-alkyl-1,2(1*H*)-diazepine derivatives. With a slight variation in work up conditions, the reaction of thiapyrylium salts **3***a* and **3***c* with methylhydrazine leads to the formation of the pyrazoline derivatives **6***a* and **6***c*, respectively; on the other hand, only pyrazolines **9***a* and **9***b* can be obtained from the corresponding reaction with phenylhydrazine. Pyrolysis of the pyrazolines **6***a*, **6***c*, **9***a*, and **9***b* provides the pyrazoles **7***a*, **7***c*, **10***a*, and **10***b*, respectively. The mechanism of some of these transformations is briefly discussed.

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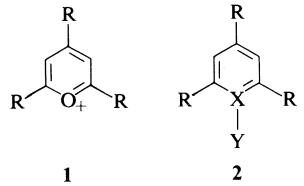
Les sels de thiapyrylium **3***a–c* réagissent avec l'hydrazine et la méthylhydrazine et donnent les triphényl-3,5,7 (4*H*) diazépines-1,2 **4***a–c* et les méthyl-1 triphényl-3,5,7 (1*H*) diazépines-1,2 **5***a–c*; les rendements de ces réactions sont bons à excellents. Bien que plusieurs (1*H*) acyl-1 diazépines-1,2 sont maintenant connues, les composés **5***a–c* représentent les premiers exemples de dérivés de type alkyl-1 (1*H*) diazépine-1,2. Avec une légère variation dans les conditions de réaction, les sels de thiapyrylium **3***a* et **3***c* réagissent avec la méthylhydrazine et donnent les dérivés de la pyrazoline **6***a* et **6***c* respectivement; par ailleurs, la réaction correspondante avec la phénylhydrazine conduit seulement aux pyrazolines **9***a* et **9***b*. La pyrolyse des pyrazolines **6***a*, **6***c*, **9***a* et **9***b* donnent respectivement les pyrazoles **7***a*, **7***c*, **10***a* et **10***b*. Le mécanisme de quelques-unes de ces transformations est brièvement discuté.

[Traduit par le journal]

The reaction of pyrylium salts with nitrogen-containing nucleophiles to yield a variety of pyridine derivatives (3) provides one of the earliest examples of interconversion of aromatic heterocyclic systems in which a one for one interchange of heteroatoms occurs:[4] **1** → **2**, X—Y = $\overset{+}{N}$—Alkyl, $\overset{+}{N}$—CH_2Ar, $\overset{+}{N}$—CH_2CO_2H (4), $\overset{+}{N}$—NHAr, $\overset{+}{N}$—NHCOR: R = NH_2, R = Ph (5), N → O (6). Analogous reactions have been shown to be useful for the conversion of pyrylium salts into sulfur and phosphorus heterocycles (**2**, XY = $\overset{+}{S}$, P) as well as benzene derivatives (**2**, X—Y = C—CO_2R, C—COMe, C—CN, C—NO_2) (3). New transformations of pyrylium salts include the following: reaction with 2-phenyl-Δ^2-oxazolin-5-one to form benzanilides (15); rearangement to 2-amino-3-aroylpyridines with cyanamide (16); ring contraction to isoxazolines with hydroxyl-



1 **2**

[1]Portions of this work have been presented at conferences (1, 2).

[2]Abstracted in part from the Ph.D. Thesis of G.Y.-P.K. submitted to the University Graduate Council, University of Waterloo, 1971.

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[4]In recent years the utility of this type of reaction with other π-isoelectronic heteroaromatic systems has been exemplified as follows: 1,2-dithiolium salts → isothiazoles (7); 1,3,5-oxadiazinium salts → aminopyrimidines (8); 1,3,4-oxadiazolium salts → *s*-triazolium salts (9); oxazolium salts → 3-imidazolines and 3-imidazolinium salts (10); 1,2,4-dithiazolium salts → 1,2,4-thiadiazoles (11,12); *N*-(4-Arylmethylene-Δ^2-oxazolin-5-ylidene) ammonium salts → 1,3-diazafulvenes (13); 1,3-oxazinium salts → pyrimidines (14).

amine hydrochloride (6, 17), to pyrazolines or pyrazoles (10, 17*b*, 18), and to pyrazolo[2,3-*a*]-quinolines (19); and ring expansion to 1,2-diazepines with hydrazines in a two for one heteroatom exchange reaction (17*a*, 18, 20*a*, 21).[5] Although the mechanism of these transformations are presumably related, evidence is available only in isolated cases (6, 17*b*).

Thiapyrylium salts would be expected to resemble pyrylium salts in their chemistry although it should be noted, perhaps surprisingly, that thiapyrylium salts have by no means received a proportionate amount of attention (3*b*, 28). Herein we report on the reaction of thiapyrylium salts (**3***a–c*) with hydrazine derivatives. When originally announced (1), some of these reactions represented the first preparations of highly unsaturated 1,2-diazepines (**4**, **5**). In the meantime, direct routes to 1,2(4*H*)-diazepines (**4**) (20*a*) and the 1-methyl-1,2(1*H*)-diazepine (**5***a*)[6] (18) from pyrylium salts have been discovered. The structural assignments (1) of **4***a* were partly based on n.m.r. characteristics which have since been extensively discussed by other investigators (20)[7] and therefore are not recapitulated here. The accompanying paper describes the protonation and acid-catalyzed rearrangement studies of these 1,2-diazepine derivatives (30).

Treatment of the triarylthiapyrylium salts **3***a–c* with an excess of hydrazine in ethanol solution gave the 1,2(4*H*)-diazepine derivatives **4***a–c* in 86–90% yield (Scheme 1). Structure assignments were based on n.m.r. spectra as indicated above and on catalytic hydrogenation of **4***a* to the known dihydrodiazepine **8** prepared from hydrazine and 1,3,5-triphenyl-1,5-pentanedione. Pyrylium salts give comparable yields of 1,2(4*H*)-diazepines (20*a*), eliminating a synthetic step, since thiapyrylium salts are prepared from pyrylium salts. Compared to these convenient reactions, thiapyrylium salts provide the 1-methyl-1,2(1*H*)-diazepines only under different and stringently controlled reaction and workup conditions. Addition of the thiapyrylium salt to an excess of neat methylhydrazine at −70° under nitrogen followed by further reaction at 0° gave the crude crystalline 1,2(1*H*)-diazepines (**5***a–c*) in 55–75% yield.[8] Analytical and spectral data (Table 1) are in full support of the proposed structures, in particular the n.m.r. spectrum of **5***a* shows the weakly coupled (J = 1.5 Hz) vinyl hydrogens, C_4- and C_6-H at 2.95 and 4.15 τ, respectively. These chemical shifts and coupling constants may be compared to similar values obtained for the elusive 2,4,6-triphenyl-1,3-oxazepine obtained but not isolated from the photolysis of 2,4,6-triphenylpyridine *N*-oxide (32). The u.v. spectra of the 1,2(1*H*)-diazepines show marked differences from those of the 1,2(4*H*)-diazepine series (20*a*), a fact which was used in support of the original structural assignments (1). Compound **5***a* was also synthesized from the 1,2(4*H*)-diazepine **4***a* and methyl iodide. The invariable production of some 2,4,6-triphenylpyridine in this reaction (see Experimental) speaks for the lability of **5***a* to thermal (18, 33) and acidic (30) conditions.

If, in the reaction of thiapyrylium salts with methylhydrazine, great care is not taken to remove excess methylhydrazine immediately after the reaction (see Experimental), the observed products are pyrazoline derivatives rather than the 1,2(1*H*)-diazepines. For example, pyrazolines **6***a* and **6***c* were obtained under these conditions. Usually the fate of the reaction could be predicted on the basis of whether oily or crystalline material was obtained directly from the reaction mixture. The oily materials obtained were mixtures of diazepine and methylhydrazine and could be shown to produce the pyrazolines upon standing and/or recrystallization (n.m.r. analysis).

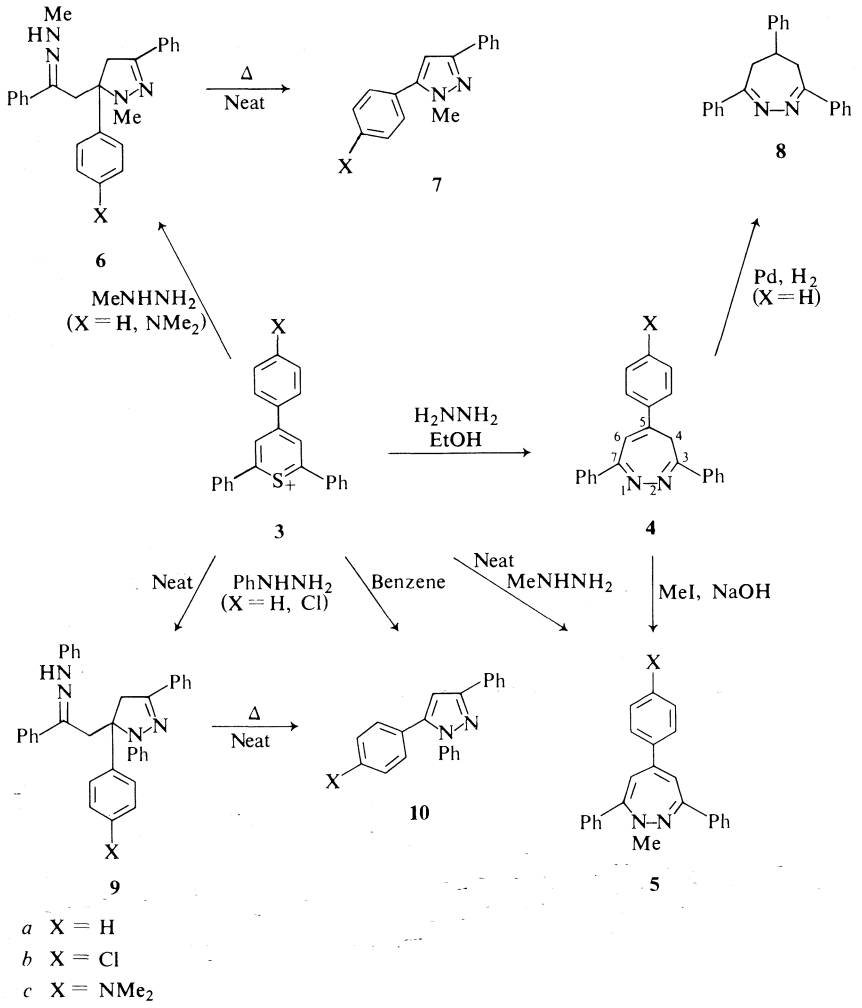
The structures of the pyrazolines **6***a*, **6***c* and **9***a*, **9***b* rest on spectral and chemical data. The mass spectrum of compound **6***a* even at low

[5]Related rearrangements and ring contractions have been observed with other heterocycles (nucleophiles): 1,2-dithiolium salts (H_2NNH_2, H_2NNHR, RSH) (7, 22, 26); 1,2,4-dithiazolium salts (KNCO) (12); 1,3,4-oxadiazolium salts (H_2NCN) (9*a*); pyrimidines and pyrimidinium salts (H_2NNH_2, H_2NNHR) (23); oxazolium salts (H_2NNHPh) (24); *N*-phenacylpyridinium ylides ($PhNHN{=}C(Cl)CO_2Et$) (25); 1,3-oxazinium salts (H_2NNH_2, H_2NOH) (14); isothiazolium salts (RNH_2, H_2NNHR, NH_2OH, $H_2N(CH_2)_2SH$, RSH, H_2S) (26); thiazolium salts (RNH_2) (27).

[6]Simple 1,2(1*H*)-diazepines are available by photolysis of *N*-iminopyridinium ylides (29).

[7]This allows unique structural assignment ruling out theoretically possible valence isomers and tautomers. A more highly substituted derivative, 3,7-bis(*p*-iodophenyl)-4,5,6-triphenyl-1,2(4*H*)-diazepine was elucidated by X-ray analysis only after several misassignments based on n.m.r. and u.v. techniques (31).

[8]These reaction conditions have not yet been consistently successful for the preparation of **5***a–c* directly from pyrylium salts; G.Y.-P. Kan and D. J. Harris. In progress.



SCHEME 1

voltages did not show a parent peak due to facile loss of acetophenone methylhydrazone to yield the pyrazole **7***a*. The n.m.r. spectrum of **6***a* showed an aliphatic proton pattern (τ 6.6, s, 2H, —CH_2C=N—, 6.5, q, 2H, J = 16 Hz, ring CH_2) which was expected on the basis of that observed for the side chain ketone corresponding to **6***a* whose structure has been established (17*b*, 18). Structures **6***a*, **6***c* and **9***a*, **9***b* were confirmed by thermolysis to the corresponding pyrazoles **7***a*, **7***c*, **10***a*, **10***b*, respectively.

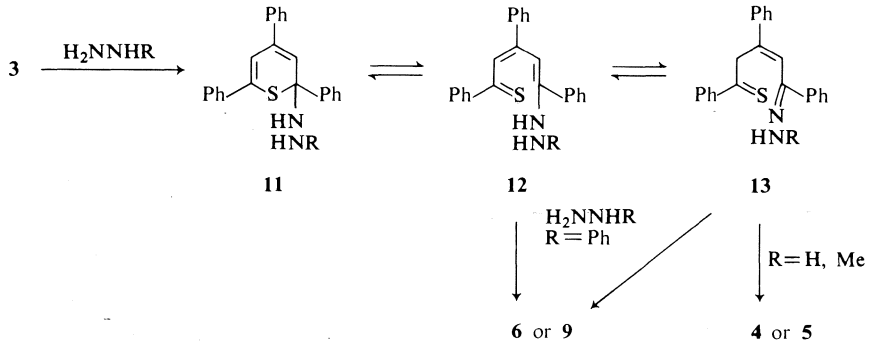
Under the conditions that afforded diazepines **5***a–c*, the reaction of **3***a* and **3***b* with phenylhydrazine unfortunately gave only the pyrazolines **9***a* and **9***b*, nor could the desired 1,3,5,7-tetraphenyl-1,2(1*H*)-diazepine be detected by n.m.r. analysis of the crude reaction product. If this reaction was carried out in benzene suspension, 1,3,5-triphenylpyrazole **10** was obtained as the only major characterizable product.

The mechanism for the formation of the observed products may be discussed by reference to the general comments advanced by Balaban (17*b*) and Buchardt and co-workers (6) for the reaction of pyrylium salts with nucleophiles (Scheme 2). Good precedent and analogy exists for the formation of α-thiapyran (**11**) (3*b*) and open-chain (**12**) (3*b*, 34) intermediates in reactions of pyrylium salts and related heterocycles. In some cases these may be isolated; in the case of thiapyrylium salts they have not been detected

TABLE 1. Ultraviolet and nuclear magnetic resonance data of 1,2(*1H*)-diazepines (**5**)

Compound	λ_{max}(EtOH) (ε) nm	τ values ($CDCl_3$) NMe[a]	C_4-H[b]	C_6-H[b]	Aromatic	Other
5*a*	407.5 (321) 270 (21 250) 225 (15 100)	7.05	4.15	2.95	2.15–2.8 (m, 15H)	
5*b*	415 (330) 275 (28 200) 222 (20 300)	7.1	4.25	2.9	2.1–2.75 (m, 14H)	
5*c*	357.5 (13 800) 266 (22 100) 222.5 (20 400)	7.05	4.10	2.9	2.0–2.7 (m, 12H)	3.25 (d, 2H, J = 8 Hz, *ortho*-H in $-C_6H_4N(CH_3)_2$), 7.0 (s, 6H, $N(CH_3)_2$).

[a]s, 3H.
[b]d, 1H, J = 1.5 Hz. This coupling was confirmed by decoupling studies.



SCHEME 2

and only the 1,2-diazepines (**4**) or pyrazolines (**6** and **9**) have been isolated. Diazepine formation may be favored by equilibration to **13** catalyzed by excess hydrazine. In the case of **13**, R = H and Me, condensation with the thioketone is facilitated by nucleophilic strength and steric factors of the juxtaposed hydrazone. In the intermediate phenylhydrazone **13**, R = Ph, however, nucleophilicity of the attacking nitrogen atom is decreased and unfavorable steric interactions due to the phenyl moiety are introduced. Consequently, a pyrazoline (**6** or **9**) is formed from **13**, R = Ph, or, more likely, from **12**, R = Ph, by an internal Michael addition mechanism. Considering the diversity of results in reactions of pyrylium and thiapyrylium salts with hydrazines (17, 18, 20*a*), it is premature to speculate on the role played by the heteroatom (oxygen *vs.* sulfur) in directing these transformations except to note that thiones are usually much more reactive towards nucleophiles than ketones (35).

Experimental

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Analysis were performed by Micro-Tech Labs., Inc., Skokie, Ill., A. B. Gygli, Toronto, Ontario, and by J. J. Kobliska, Analytical Laboratories, American Cyanamid Co. The i.r. spectra were recorded on Beckman IR-5A and -10 instruments in chloroform solution unless otherwise noted. The u.v. spectra were measured on a Beckman DB-G spectrophotometer in ethanol solution unless otherwise indicated. The n.m.r. spectra were recorded on Varian T-60 and HA-100 and Perkin-Elmer R-12B spectrometers in deuteriochloroform solution unless otherwise stated using TMS as internal standard. Spectra listed follow the order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), number of protons, coupling constant (Hz), and assignment. Mass spectra were determined with Hitachi-Perkin Elmer RMU-6E and MS-30 spectrometers. Thin-layer, preparative thick-layer, and column chromatography were performed with silica gel specified for these purposes and obtained from Brinkmann (Canada) Ltd.

Thiapyrylium Salts (3a–c)

These were prepared by the method of Wizinger and Ulrich (36).

2,4,6-Triphenylthiapyrylium Fluoroborate (3a).

This was obtained in 80% yield. A sample recrystallized from acetic acid showed m.p. 201–202.5° (lit. (28*c*) m.p. 218°, (40) m.p. 196.5–197.5°).

4-(p-Chlorophenyl)-2,6-diphenylthiapyrylium Fluoroborate (3b).

This was obtained in 72% yield after recrystallization from acetic acid, m.p. 143–146°.

Anal. Calcd. for $C_{23}H_{16}SClBF_4$: C, 61.81; H, 3.58; S, 7.17. Found: C, 61.52; H, 3.42; S, 6.82.

4-(p-Dimethylaminophenyl)-2,6-diphenylthiapyrylium Perchlorate (3c).

This was obtained in 88% yield after recrystallization from acetic acid, m.p. 256–258° (lit. (36), m.p. 247–249°, (37) 256–258°).

1,2(4H)-Diazepines (4a–c)

3,5,7-Triphenyl-1,2(4H)-diazepine (4a)[1]

Two hundred milliliters of 100% hydrazine hydrate (87-fold excess) was stirred at room temperature while 20.0 g (0.048 mol) of 2,4,6-triphenylthiapyrylium perchlorate (36) was sifted in during 1/2 h. Stirring was continued overnight, the product then being filtered, washed with water, and dried. Crystallization from 800 ml of methylcyclohexane (Darco) gave 9.0 g (59%) of pale yellow product, m.p. 186–190°. Recrystallization from acetonitrile gave colorless crystals, m.p. 195–196° (lit. (20*a*) m.p. 191–192°).

When the reaction was carried out under the conditions of Buchardt *et al.* (20*a*), an 89% yield of **4***a* was obtained.

The bright yellow picrate of **4***a* was prepared in butanol and crystallized from alcohol; m.p. 198–200.5°.

Anal. Calcd. for $C_{29}H_{21}N_5O_7$: C, 63.1; H, 3.8; N, 12.7. Found: C, 62.9; H, 3.7; N, 12.8.

Compounds **4***b* and **4***c* were prepared according to the conditions of Buchardt *et al.* (20*a*).

5-(p-Chlorophenyl)-3,7-diphenyl-1,2(4H)-diazepine (4b).

This was obtained in 86% yield. A sample recrystallized from acetonitrile showed m.p. 190–191.5° (lit. (20*a*) m.p. 188–189°).

5-(p-Dimethylaminophenyl)-3,7-diphenyl-1,2(4H)-diazepine (4c).

This was obtained in 90% yield and recrystallized from acetonitrile for analysis, m.p. 216.5–218°.

Anal. Calcd. for $C_{25}H_{23}N_3$: C, 82.2; H, 6.3; N, 11.5. Found: C, 81.9; H, 6.5; N, 11.5.

The picrate of **4***c* was prepared in butanol and crystallized from the same solvent as bronze needles, m.p. 217.5–219.5° (dec.).

Anal. Calcd. for $C_{31}H_{26}N_6O_7$: C, 62.6; H, 4.5; N, 14.1. Found: C, 62.9; H, 4.4; N, 14.3.

Hydrogenation of 4a to 4,5-Dihydro-3,5,7-triphenyl-1,2-(6H)-diazepine (8)

Compound **4***a* (0.141 g, 4.37 mmol) in 35 ml of absolute ethanol was hydrogenated at atmospheric pressure in the presence of *ca.* 70 mg of 5% palladium on charcoal. Hydrogenation was stopped after absorption of approximately 5.25 mmol of hydrogen. The solution was filtered and the filtrate concentrated *in vacuo*. The residue was passed through a column of silica gel to yield 0.091 g (64%) of colorless compound **8**, m.p. 159–161°, identical by mixture m.p. and n.m.r. comparison with an authentic sample prepared according to Amiet and Johns (38).

1,2(1H)-Diazepines (5a–c)

1-Methyl-3,5,7-triphenyl-1,2(1H)-diazepine (5a)

The apparatus consisted of a two-necked flask equipped with a drying tube and an attachment for addition of solid (39). The flask was charged with neat methylhydrazine (10 ml) and the attachment was charged with thiapyrylium salt **3***a* (4.0 g, 10 mmol). After the flask was immersed in a liquid nitrogen bath, compound **3***a* was sifted in over a few minutes. The mixture was allowed to warm to 0° and was stored at this temperature for 13 h. The resulting red crystals (2.55 g, 65%) were collected by filtration and were dried under high vacuum. Careful recrystallization from ethanol or methylcyclohexane at room temperature or below gave burgundy red crystals of **5***a*, m.p. 116.5–118°; mass spectrum (*m/e*, % relative intensity) 336 (M^+, 14), 308(21), 307(48), 306(21), 234(29), 233(100).

Anal. Calcd. for $C_{24}H_{20}N_2$: C, 85.7; H, 6.0; N, 8.3. Found: C, 85.6; H, 6.1; N, 8.2.

Compounds **5***b* and **5***c* were prepared by the above procedure.

1-Methyl-5-(p-chlorophenyl)-3,7-diphenyl-1,2(1H)-diazepine (5b)

This was obtained in 74% yield. Recrystallization from methylcyclohexane and then from ethanol gave an analytical sample, m.p. 132.5–133.5°; mass spectrum (*m/e*, relative intensity) 370.5 (M^+, 18), 369(18), 343(23), 342(23), 341(50), 306(23), 269(36), 268(27), 267(100), 118(45).

Anal. Calcd. for $C_{24}H_{19}N_2Cl$: C, 77.73; H, 5.13; N, 7.56. Found: C, 77.74; H, 4.96; N, 7.63.

1-Methyl-5-(p-dimethylaminophenyl)-3,7-diphenyl-1,2-(1H)-diazepine (5c)

This was obtained in 68% yield. Successive recrystallization from methylcyclohexane and ethanol provided an analytical sample, m.p. 126–127°; mass spectrum (*m/e*, % relative intensity) 379 (M^+, 10), 378(10), 351(30), 350(100), 349(30), 277(23), 276(70), 103(41).

Anal. Calcd. for $C_{26}H_{25}N_3$: C, 82.29; H, 6.64; N, 11.07. Found: C, 82.50; H, 6.75; N, 11.11.

Preparation of 1-Methyl-3,5,7-triphenyl-1,2(1H)-diazepine (5a) from 4a

A mixture of **4***a* (0.190 g, 0.59 mmol), methyl iodide (6 ml), and pulverized sodium hydroxide (0.250 g, 6.25 mmol) was stirred at room temperature for 24 h. The solid was removed by filtration and the filtrate was concentrated to yield a gum (0.229 g) which was subjected to preparative thick-layer chromatography (CH_2Cl_2) to afford 2,4,6-triphenylpyridine (6%) and compound **5***a* (70%) which were shown to be identical to authentic materials by n.m.r., m.p., and mixture m.p. comparison.

Formation of Pyrazoline Derivatives 6a, 6c, and 9a, 9b

The instability of the pyrazoline derivatives described below precluded elemental analysis.

1-Methyl-3,5-diphenyl-5-phenacyl-2-pyrazoline Methylhydrazone (6a)

The apparatus which was described in connection with the preparation of compound **5***a* was used. To methylhydrazine (10 ml) that had been frozen to a glass in liquid nitrogen was added 2,4,6-triphenylthiapyrylium fluoroborate (**3***a*) (2g, 4.85 mmol) under anhydrous conditions. The mixture was allowed to warm to 0°. The resulting red solution was stored at this temperature and deposited,

over 13 h., a red gum which was collected by filtration. The gum was recrystallized from hot ethanol to give 1.1 g (29%) of **6***a*, m.p. 135° (dec.); n.m.r. τ 2.2–2.9 (m, 15H, aromatics), 3.1 (br s, 1H, NH, exchanged with D_2O), 6.6 (s, 2H, side-chain CH_2), 6.5 (q, 2H, J = 16 Hz, CH_2), 7.05 (s, 3H, side-chain NCH_3), 7.3 (s, 3H, NCH_3); mass spectrum at <10 eV, 80° inlet temperature (*m/e*, % relative intensity) 234 ($M^+ - C_6H_5C(=NNHCH_3)CH_3$, 100), 233(27), 148(50), 147(27), 118(39).

*1-Methyl-3-phenyl-5-(p-dimethylaminophenyl)-5-phenacyl-2-pyrazoline Methylhydrazone (**6c**)*

This compound was obtained under conditions similar to those described for the formation of **6***a*, m.p. 118–120° (dec.); n.m.r. τ 2.2–2.9 (m, 13H, aromatic and NH (exchangeable with D_2O) protons), 3.3 (d, 2H, J = 8 Hz, *ortho*-H of dimethylaminophenyl ring), 6.6 (s, 2H, side-chain CH_2), 6.4 (q, 2H, J = 15 Hz, CH_2), 6.95 (s, 3H, side-chain NCH_3), 7.0 (s, 6H, $N(CH_3)_2$), 7.22 (s, 3H, NCH_3); mass spectrum at <10 eV, 80° inlet temperature (*m/e*, % relative intensity) 277 ($M^+ - C_6H_5C(=N—NHCH_3)CH_3$, 100), 276(20), 148(47), 119(36), 118(55).

*1,3,5-Triphenyl-5-phenacyl-2-pyrazoline Phenylhydrazone (**9a**)*

To phenylhydrazine (2.16 g, 19 mmol) which had been frozen to a glass in liquid nitrogen was added 2,4,6-triphenylthiapyrylium fluoroborate (**3***a*) (4g, 9.6 mmol) and the mixture was set aside at room temperature for one week. The solid was collected by filtration and recrystallized from ethanol to give 1.3 g (26%) of **9***a*, m.p. 101–104°; n.m.r. τ 2.26–3.41 (m, 26H, aromatic and NH (exchangeable with D_2O) protons), 6.14 (s, 2H, side-chain CH_2), 6.65 (q, 2H, J = 18 Hz, CH_2); mass spectrum at <10 eV, 80° inlet temperature (*m/e*, % relative intensity) 296 ($M^+ - C_6H_5C(=NNHC_6H_5)CH_3$, 50), 295(28), 210(36), 105(64), 104(64), 103(100).

*5-p-Chlorophenyl-1,3-diphenyl-5-phenacyl-2-pyrazoline Phenylhydrazone (**9b**)*

This compound was obtained in 20% yield by the method described for the preparation of **9***a*, m.p. 110° (dec.); n.m.r. τ 2.2–3.6 (m, 26H, aromatic and NH (exchangeable with D_2O) protons), 6.1 (s, 2H, side-chain CH_2), 6.65 (q, 2H, J = 17 Hz, CH_2); mass spectrum *m/e*, % relative intensity 330.5 ($M^+ - C_6H_5C(=NNHC_6H_5)CH_3$, 50), 329.5(22), 210(100), 119(57).

*Thermolysis of Pyrazolines **6a**, **6c**, **9a**, and **9b** to Pyrazoles **7a**, **7c**, **10a**, and **10b***

Compound **6***a* (173 mg, 0.45 mmol) was pyrolyzed at its melting point in a sealed tube inserted in an oil bath (135°) for 25 min to give after column chromatography (benzene) 98 mg (91%) of *1-methyl-3,5-diphenylpyrazole* (**7***a*), m.p. 52–54° which was shown to be identical by mixture m.p. determination to an authentic sample prepared by a literature procedure (41).

Under the above conditions, pyrazoline **6***c* gave *1-methyl-3-phenyl-5-(p-dimethylaminophenyl)pyrazole* (**7***c*) in 81% yield, m.p. 98.5–99.5°; n.m.r. τ 2.12 and 2.65 (m, 7H, aromatics), 3.23 (d, 2H, J = 7.5 Hz, *ortho*-H of dimethylaminophenyl ring), 3.46 (s, 1H, pyrazole ring H) 6.09 (s, 3H, NCH_3), 7.02 (s, 6H, $N(CH_3)_2$); mass spectrum (*m/e*, % relative intensity) 277 (M^+, 100), 276(21), 263(32), 167(26), 149(74).

Anal. Calcd. for $C_{18}H_{19}N_3$: C, 77.95; H, 6.90; N, 15.15. Found: C, 77.38; H, 6.99; N, 15.09.

Pyrolysis of **9***a* gave *1,3,5-triphenylpyrazole* (**10***a*) in 68% yield, m.p. 136–140° shown to be identical by mixture m.p. determination to an authentic sample obtained by a literature method (42).

Pyrolysis of **9***b* gave *5-(p-chlorophenyl)-1,3-diphenylpyrazole* (**10***b*) in 60% yield, m.p. 112–114°; lit. (22*c*) m.p. 113–115°; n.m.r. τ 1.8–2.15 and 2.3–2.75 (m, 2H, and 12H, aromatics), 3.15 (s, 1H, pyrazole ring H).

*Direct Formation of 1,3,5-Triphenylpyrazole (**10a**)*

To a suspension of 2,4,6-triphenylthiapyrylium fluoroborate (**3***a*) (2.0 g, 4.8 mmol) in benzene (150 ml) was added phenylhydrazine (1.08 g, 10 mmol) and the mixture was stirred at room temperature overnight. The mixture was evaporated to dryness *in vacuo* and the resulting oil was passed through a short column of silica gel (benzene) to afford 0.97 g (67%) of **10***a* identical to an authentic sample (42) by mixture m.p. determination.

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